

University of Groningen

Experimental study of the effect of bubbles, drops and particles on the product distribution for a mixing sensitive, parallel-consecutive reaction system

Brilman, D.W.F.; Antink, R.; Swaaij, W.P.M. van; Versteeg, G.F.

Published in:
Chemical Engineering Science

DOI:
[10.1016/S0009-2509\(98\)00298-X](https://doi.org/10.1016/S0009-2509(98)00298-X)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1999

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Brilman, D. W. F., Antink, R., Swaaij, W. P. M. V., & Versteeg, G. F. (1999). Experimental study of the effect of bubbles, drops and particles on the product distribution for a mixing sensitive, parallel-consecutive reaction system. *Chemical Engineering Science*, 54(13), 2325-2337. [https://doi.org/10.1016/S0009-2509\(98\)00298-X](https://doi.org/10.1016/S0009-2509(98)00298-X)

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.



Experimental study of the effect of bubbles, drops and particles on the product distribution for a mixing sensitive, parallel-consecutive reaction system

D.W.F. Brilman*, R. Antink, W.P.M. van Swaaij, G.F. Versteeg

Department of Chemical Engineering, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands

Abstract

For stirred multiphase reactors the effect of a dispersed (gas, liquid or solid) phase on the product distribution for a mixing sensitive reaction was tested. Turbulence modification due to the presence of dispersed-phase particles has been reported frequently in literature, but the extent of the effect in a stirred multiphase reactor was not clear. In this work the well-known mixing sensitive diazo-coupling reaction system was selected to investigate the influence of the changes in the turbulent kinetic energy spectrum on the product distribution. This reaction system was found to be suitable to study the influence of a dispersed (gas, liquid or solid) phase. The Engulfment model could describe the single-phase experiments and describes reasonably well the multiphase experiments when the effective dispersion properties are implemented. For the liquid–liquid dispersions effects of de-localization of the reaction zone were encountered, due to Naphthol extraction by the dispersed phase. The Engulfment model was extended to incorporate mass transfer and the first experimental and simulation results are promising. Additional, experimental and theoretical, research studying the combined effects of the mass transfer rate and the mixing rate for the liquid–liquid dispersions is highly desired. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Mixing; Multiphase; Experimental study; Chemical reaction

1. Introduction

In multiphase reaction systems with multiple, (ir)-reversible, chemical reactions mass transfer, mixing and chemical reaction rate determine in an open competition the conversion rate and also the final product distribution. An example of such a complex multiphase reaction system is the Koch carbonylation of olefinic compounds to produce carboxylic acids (Falbe, 1980). This complex gas–liquid–liquid reaction system is operated on industrial scale in a stirred liquid phase, pressurized reactor. Apart from the desired reaction, the acid-catalyzed addition of carbon monoxide to an olefin, undesired olefin polymerization may occur. On analyzing this situation, the question rose to what extent the mixing in the continuous liquid phase near the feedpoint of the

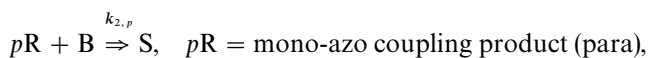
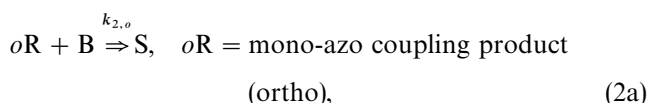
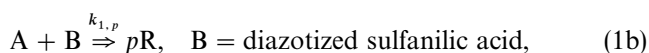
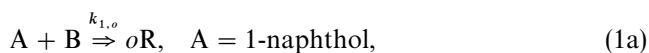
olefinic reactant (and with this, the product distribution) was affected by the presence of a dispersed (liquid) phase. A second important issue is the interaction between mixing and mass transfer between the continuous liquid phase and the dispersed liquid phase in the zones neighboring the feedpoint. An experimental study investigating the extent of these influences, also at higher volume fractions dispersed phase, using a well-known model reaction system, as the diazo-coupling reaction proposed by Bourne et al. (1981), was considered suitable to study these (micro-)mixing phenomena.

For a complex reaction system with fast chemical reactions in a parallel-consecutive reaction scheme as, e.g.: $A + B \rightarrow P$, $P + B \rightarrow X$ the production of component X depends on the local concentrations of B and P in the reaction zone. In case of poor mixing characteristics at the molecular scale local concentrations of B near its feedpoint in the reactor may differ significantly from its (bulk phase) average value, leading

*Corresponding author. Tel.: 0031 534894479, fax: 0031 534894774.

to an increase of the production of the consecutive reaction product X.

The micromixing process can be studied experimentally by using chemical test reactions. The diazo-coupling reaction of Bourne et al. (1981), for which the reaction kinetics are well established (Bourne et al., 1990), is frequently used for this purpose. This reaction system consist of a set parallel, consecutive instantaneously fast, irreversible reactions, see Eqs. (1) and (2):



Usually the reaction system is operated semi-batch wise. Reactant B is added slowly to the reaction mixture, containing an excess of reactant A, where B is rapidly converted into the mono azocompounds (*oR*, *pR*) and the bis-azocompound S. The product distribution is uniquely characterized by the product ratio X_S , representing the selectivity of component B towards product S, given in Eq. (3).

$$X_S = \frac{2[S]}{2[S] + [oR] + [pR]}. \quad (3)$$

Mixing may affect the product distribution parameter X_S , significantly. In a well mixed reactor (at high energy dissipation levels) almost exclusively mono-azo coupling products will be formed and, consequently, the X_S value will be low.

The process of mixing a reactant into a bulk phase can be considered at different scales, starting with the spatially distribution of feed lumps through the bulk phase (macromixing), followed by reduction of the scale of the unmixed lumps by breakage without influence on molecular mixing (mesomixing). The smaller fluid elements are subjected to laminar strain and molecular diffusion becomes more and more important with decreasing characteristic length scale (micromixing). Finally, homogeneity at the molecular scale is rapidly attained through molecular diffusion.

The mixing process can be related to turbulent energy spectrum (the distribution of turbulent energy over the

eddy length scale) of the bulk liquid phase, see, e.g. Baldyga and Pohorecki (1995) for an overview. The viscous-convective deformation of fluid lumps, which increases the effect of concentration variance dissipation by molecular diffusion, is considered to be the most important micromixing feature.

The reactant concentration in the reaction zone can be influenced by macroscale, mesoscale and microscale effects. To interpret the experimentally determined product distribution in terms of micromixing characteristics, the macroscale and mesoscale mixing effects need to be excluded. This can be checked experimentally by varying the feed time of the (fixed amount of) reactant B containing solution. For a semi-batch reactor a critical feed time can be observed, above which the product distribution is no longer sensitive to the feed time (Bourne and Thoma, 1991). Under these conditions the product distribution is determined by the micromixing processes of fluid element deformation and molecular diffusion in the viscous-convective and viscous-diffusive subranges of the turbulent energy spectrum. Since these processes are governed by the energy dissipation rates and fluid viscosity, local energy dissipation rates can be determined.

2. Theory

2.1. Single-phase-systems

The micromixing process is determined by viscous deformations of fluid feed lump elements and molecular diffusion. The rate of viscous deformation of the fluid elements is generally assumed to be proportional to $(\epsilon/\nu)^{1/2}$, the Kolmogoroff rate of strain in the viscous subrange. Due to turbulent vorticity the long thin slabs of the deforming fluid lump are twisted and fluid from the environment is incorporated. Now thin lamellar structures are formed in which high concentration gradients are formed by viscous deformation. In these structures, concentration variances are rapidly dissipated by molecular diffusion, thereby losing the lamellar character. For not too high Schmidt numbers (Sc) the diffusion process is faster than the rate of incorporation of fluid from the environment, called “Engulfment”, and this engulfment process is dominating micromixing (Baldyga and Pohorecki, 1995).

The single-phase experiments with the diazo-coupling test reaction presented in this work are conducted in the regime where the Engulfment model, *E-model* (Baldyga and Bourne, 1989) can be used to describe the micromixing process. Due to incorporation of fluid from the environment the feed lumps grow at the expense of the environment and the concentration in the reaction zone changes due to chemical reaction and mixing with bulk fluid-phase elements of equal

volume:

$$\frac{dc_i}{dt} = E(c_{\text{bulk},i} - c_i) - R_i. \quad (4)$$

The engulfment rate, E , is the main parameter in this model and is related to the local energy dissipation rate by

$$E \approx 0.058 \left(\frac{\varepsilon}{\nu} \right)^{0.5} = 0.058 \left(\frac{\varepsilon \rho}{\mu} \right)^{0.5}. \quad (5)$$

From experimentally determined product distributions (X_S values), using the E-model by Baldyga and Bourne (1989), the local energy dissipation rates in the reaction zone can be derived. Since the relative energy dissipation in an agitated vessel may vary strongly with position, it is important to ensure that the reaction is completed in a zone of more or less homogeneous energy dissipation rate. Otherwise, the trajectory of a feed lump through zones of different energy dissipation levels needs to be considered (Baldyga and Bourne, 1988).

2.2. Turbulence modification by particles

For multiphase systems, the presence of dispersed-phase particles may influence the macroscale continuous-phase hydrodynamics as well as the turbulent energy spectrum, and thus mixing at different scales. Depending on holdup, particle size and -density the particles may interact with the macroscale fluctuations thereby extracting energy from the average flow and increasing high-frequency turbulence by vortex shedding ('turbulence production'). Small, light particles will tend to interact with high-frequency microscale fluctuations. Turbulent kinetic energy is dissipated for the acceleration of dispersed-phase particles ('turbulence damping').

Gore and Crowe (1989) and Hetsroni (1989) reviewed the limited amount of available experimental data on turbulence modification by (dispersed) particles. The results, mainly obtained for gas–solid and a few for gas–liquid systems at low particle loadings, were interpreted differently. Gore and Crowe (1989) proposed that the way in which the turbulence level is modified solely depends on the particle size; 'small particles' with respect to the turbulence length scale pick up energy from the turbulent eddies and thus decrease the turbulence level, whereas 'large particles' cause significant vortex shedding, thereby increasing the turbulence. From their data correlation it seems that the turbulence damping effect is marginally, whereas the turbulence increase by larger particles is more pronounced. Hetsroni (1989) used the particle Reynolds number to correlate essentially the same set of data. Particles with small Reynolds numbers (< 400) were considered to suppress turbulence, whereas

particles under high particle Reynolds number increased the turbulence levels.

Modification of the turbulence kinetic energy spectrum for a continuous *liquid* phase by solid particles has been studied experimentally very scarcely. Kada and Hanratty (1960) studied the effect of solid particles on turbulent diffusion of injected KCl pulses for slurry systems falling through a vertical pipe. They found that solids did not have a large effect on the turbulence level, except for solids having an appreciable slip velocity (high density and/or relatively large (for glass spheres $> 300 \mu\text{m}$) and at sufficiently high solids concentrations (2–3 vol% for glass spheres)). At these conditions the turbulent eddy diffusivity calculated increased 2.5 times.

Schreck and Kleis (1993) presented a comprehensive study on the effect of solid spherical particles (600–700 μm , plastic ($\rho_p = 1049 \text{ kg/m}^3$) and glass ($\rho_p = 2500 \text{ kg/m}^3$)) on grid-generated liquid-phase turbulence. In their study a monotonic increase in energy dissipation rate with particle concentration was observed. The additional energy dissipation rate for the glass particles was almost two times that of the light plastic particles. From the literature overview by Schreck and Kleis (1993) it is clear that the addition of solid particles may indeed modify the turbulence spectrum (and thus affect mixing). For gas–solid two-phase flow, experimentally both the effects of increasing turbulence for large particles ($\approx 1 \text{ mm}$) and decreasing turbulence for small particles ($\approx 200 \mu\text{m}$) have been reported (Tsuji et al., 1984). For turbulent pipeflow it was found that intermediate sized particles ($\approx 500 \mu\text{m}$) increased turbulence at the pipe center and reduced it along the wall. Both from the work of Schreck and Kleis (1993) and of Tsuji et al. (1984) for gas–solid two phase flow it is clear that the isotropy of the flow is enhanced due to the presence of particles.

Elgobashi (1994) presented a regime map for turbulent fluid–solids flow to discriminate between regimes in which turbulence is enhanced and suppressed, based on the solids holdup and the ratio of the particle response time τ_p and the Kolmogoroff time scale τ_K (turbulence enhancement for $\tau_p/\tau_K > 10^2$). Turbulence enhancement by vortex shedding will occur at high particle Reynolds numbers (> 400), requiring relatively large particles and high density differences. Turbulence damping may be caused by energy dissipation through fluid-particle interaction (energy required for suspending and oscillating the particles due to continuous phase turbulence, 'two way coupling'), particle-particle interaction (so-called 'four-way coupling') and due to the fact that in dense solutions a significant fraction of the fluid is present as low turbulent added mass moving with the particles. According to Elgobashi's classification all the results presented in this present study were carried out in the

four-way coupling regime (dispersed phase holdup > 0.1 vol%).

Summarizing, it can be concluded that particles modify the turbulence energy spectrum, e.g. by facilitating energy transfer from large to smaller eddies and promoting isotropy of the turbulence. The effect, however, on energy dissipation rate and mixing on a scale, which is relevant to a complex chemical reaction, cannot be derived from these studies.

In a few studies the aspect of the influence of particles on the product distribution for a mixing sensitive (homogeneous) chemical reaction has been considered. Bennington and Bourne (1990) and Bennington and Thangavel (1993) used the diazo-coupling reaction of Bourne et al. (1981) to study the effect of suspended nylon fibers on macromixing and micromixing in a stirred tank. They found that the fibers, irrespective of changes to macroscopic flow patterns, dampen the observed turbulence level, which was assumed to be caused by network formation by the fibers.

Villiermaux et al. (1994) used a parallel (iodine–iodate) reaction system to study the effect of suspended solids and inert bubbles on micromixing in stirred reactors. Preliminary results showed that the effect of solids ($< 40 \mu\text{m}$) was considerable. Micromixing seemed to be enhanced significantly as a strong increase of micromixedness was observed at only 4 wt% addition of solid particles. In a consecutive publication by Guichardon et al. (1995) the preliminary results of Villiermaux et al. (1994) were considered to be invalid. After checking the mass balance more precisely and re-investigation of the reaction kinetics only a minor effect of the presence of particles in this latter paper remained. This example illustrates that especially for multiphase systems the reaction kinetics for the test system as well as effects of product adsorption or absorption in the dispersed phase should be known. Guichardon et al. (1995) stressed the need for a study of more concentrated suspensions.

More recently, Barresi (1997) studied the influence of solid particles on the product distribution obtained for a fast, parallel reaction scheme. Two preliminary conclusions were presented, the first being that the particles had only an effect at relatively high volume fractions (> 10 vol%) and, secondly, it was found for three experiments at constant volumetric holdup that large glass particles (425–500 μm) exhibited a significant influence on the product distribution, whereas fine glass particles (100–177 μm) and PET beads (having a equivalent diameter of 3 mm) had a minor effect and no effect on the product distribution respectively.

In the present study attention will be focussed at high dispersed phase holdups. Since for a dispersed liquid phase mass transfer may be important, an inert solid and gas phase were also used, to study the effect of dispersed holdup and ‘particle’ size. Macroscopically, the effects of

a dispersed phase on turbulence may be noticeable via, e.g. the effective viscosity and density of the dispersion. In interpreting the experimental data the E-model, valid for a single phase situation, is used to see if macroscopic physical properties for the dispersion are able to describe the observed trends in the product distribution with increasing holdup.

2.3. Interpretation of experimental results for multiphase systems using the E-model

Although the E-model is derived for single-phase systems, the model will be used to interpret the experimental data for the multiphase systems used. It will be tested if the E-model, using the apparent slurry viscosity and slurry density, can be used to describe the obtained product distributions at changing operating conditions, like dispersed phase holdup. The power input via the impeller and the average energy dissipation rate ε (W/kg) are given by

$$P = C\rho_{\text{eff}}N^3d_{\text{st}}^5 \quad (\text{W}), \quad (6)$$

$$\varepsilon_{\text{eff}} = \frac{P}{(\rho_{\text{eff}}V)} = \frac{CN^3d_{\text{st}}^5}{V} \quad (\text{W/kg dispersion}). \quad (7)$$

For the kinematic viscosity ν (m^2/s) $= \mu/\rho$, the change in viscosity was taken into account via correlations for the relative dynamic viscosity (μ_r) of liquid–solid and liquid–liquid dispersions at different volumetric holdups. For modeling the liquid–solid dispersions the correlation of Graham (1981) was used for estimating μ_r . For the effective viscosity of liquid–liquid dispersions the correlation of Vermeulen (Perry, 1988; Eqs. (21)–(32)) was compared with the Graham correlation, which may be applicable at low holdups since the droplets are small and rigid and will probably behave as solid spheres. The density ρ in Eq. (5) was taken equal to the effective dispersion density and to the continuous-phase density, leading to two definitions of the Engulfment parameter E which were used in the simulations:

$$E(\text{I}) = 0.058 \left(\frac{\varepsilon_R \varepsilon_{\text{av}}}{\nu} \right) = 0.058 \left(\frac{\varepsilon_R CN^3 d_{\text{st}}^5 \rho_{\text{eff}}}{V \mu_{\text{eff}}} \right), \quad (8)$$

$$E(\text{II}) = 0.058 \left(\frac{\varepsilon_R \varepsilon_{\text{av}}}{\nu} \right) = 0.058 \left(\frac{\varepsilon_R CN^3 d_{\text{st}}^5 \rho}{V \mu} \right), \quad (9)$$

For the experiments with a dispersed liquid phase the E-model was extended to incorporate mass transfer between the bulk of the continuous liquid phase and the dispersed liquid phase, both considered to be ideally mixed. The set of additional mass transfer model

equations is

$$V_{\text{bulk}} \frac{dc_{c,i}}{dt} = k_{\text{LL}} A_{\text{LL}} \left(\frac{c_{d,i}}{m_i} - c_{c,i} \right) \quad (\text{continuous phase}) \quad (10)$$

$$V_d \frac{dc_{d,i}}{dt} = k_{\text{LL}} A_{\text{LL}} \left(c_{c,i} - \frac{c_{d,i}}{m_i} \right) \quad (\text{dispersed phase}) \quad (11)$$

In the present contribution, mass transfer was accounted for discontinuously by calculating the exchange between the two liquid phases after each (of the σ) feed lump(s) during t_{feed}/σ (s). The overall mass transfer coefficient k_{LL} was estimated conservatively from the partial coefficients for mass transfer inside and outside the droplets by assuming stagnant media; thus $Sh_{\text{inside}} = 2\pi^2/3$ is used for mass transfer inside the droplets and $Sh_{\text{outside}} = 2$ for the external partial mass transfer coefficient, thereby using $D = 1 \times 10^{-9} \text{ m}^2/\text{s}$ as typical liquid-phase diffusion coefficient. The interfacial area A_{LL} was calculated using $A_{\text{LL}} = 6V_d/d_p$ and the correlation of Calderbank for the drop size.

The effect of mass transfer can be estimated by comparing the timescale for mass transfer ($k_{\text{LL}} A_{\text{LL}}/V_{\text{bulk}}$) with the time for complete engulfment of a feedlump. Depending on initial conditions and the distribution coefficients for Naphthol mass transfer from the dispersed phase may become the limiting process. In that case the current method of solving the equations must be adapted.

3. Experimental

For the mixing experiments a baffled, flat bottom, stirred tank was used as reactor, equipped with a six blade Rushton-like turbine (see Fig. 1). The feed points are indicated in the figure, as well as all relevant dimensions. Feedpoint A is located at the top of the plane of the stirrer (radial flow zone). Feedpoints B, C and D are located just above the stirrer, in the suction stream to the impeller zone. Feedpoint E is located in a stream leaving the stirrer zone where axial flow dominates. To avoid backmixing of bulk reaction liquid into the feedpipe a small diameter of the feedpipe was chosen (inner diameter: 1 mm). This diameter was shown to be sufficient small using the criteria presented by Baldyga and Pohorecki (1995).

3.1. Development of the test reaction system

In most experiment series the 1-Naphthol reaction system represented by Eqs. (1) and (2) is used. For some experiments the extended reaction system of Bourne et al. (1992), developed for high energy dissipation rates was used. This system encompasses reactions (1) and (2), as

well as a parallel reaction of 2-Naphthol (AA) with diazotized sulfanilic acid.



The product distribution is then characterized by $X_{\text{S'}}$ and X_{Q} , which are defined below.

$$X_{\text{S'}} = \frac{2[\text{S}]}{[\text{oR}] + [\text{pR}] + 2[\text{2}] + [\text{Q}]}, \quad (13a)$$

$$X_{\text{Q}} = \frac{[\text{Q}]}{[\text{oR}] + [\text{pR}] + 2[\text{2}] + [\text{Q}]}. \quad (13b)$$

Before using the reaction system of Bourne et al. (1981), the UV-extinction coefficients as reported by Lenzner (1991) were verified. Therefore, the reaction product pR was synthesized, identified by NMR and purified by several washing and recrystallisation steps. The UV-extinction coefficients as reported by Lenzner (1991) were confirmed for pR . From other syntheses the products oR , S and Q were obtained at purity levels of 90–95% by element analysis, but it turned out to be difficult to improve on the purity. The UV-extinction coefficients were, however, conform the purity level and the extinction coefficients reported by Lenzner (1991), thus justifying the use of the extinction coefficients reported by Lenzner (1991).

Naphthols (1- and 2-) and sulfanilic acid of 99 + % purity were purchased from Acros Organics, as well as the Sodium Carbonate and Sodium Bicarbonate for the buffer solution ($\text{pH} = 9.9$). The reactant B (diazotized sulfanilic acid) was obtained almost quantitatively, according to a test based on the Sandmeyer reaction. The occurrence of degradation of reaction products, diluted $50\times$ for UV analysis, was found to be negligible. Stability was also tested for 1- and 2-Naphthol solutions and for a solution of freshly synthesized diazotized sulfanilic acid. 2-Naphthol solutions (1% degradation in 20 h) was found to be much more stable than the 1-Naphthol solutions (5% in 6 h) and the 1- + 2-Naphthol mixtures. Sparging nitrogen through the naphthol solution improves the stability. 1-Naphthol was dissolved for each experiment in a series separately just before the experimental usage. By storing the diazotized sulfanilic acid solutions in an ice-bath the degradation of diazotized sulfanilic acid during one experiment series (ca. 5 h) could be reduced to ca. 1%.

3.2. Analysis

Multicomponent regression (over the range of 400–600 nm) was used to obtain the individual component concentrations from the recorded UV spectrum (HP 8452A spectro photometer). The regression coefficients were usually better than 0.9995. Tests with small shifts in

the UV spectrum showed that the *o*R/*p*R distribution is relatively sensitive to this, however, the segregation index X_S remains almost unaffected. The presence of small amounts of dissolved octanol and heptane in the analysis samples (reactor samples, diluted $50\times$ with buffer solution) did not affect the UV-analysis. For single-phase experiments no effect was found in experiments in which the Naphthol/buffer solution was saturated with heptane or octanol.

3.3. Accuracy

Reproducibility of the X_S value for experiments within a series (measured at sequentially) at the same feedpoint was tested for the 1-Naphthol and 1- + 2-Naphthol system. Standard deviation values for a series of experiments under identical conditions revealed that $X_S \approx 0.092 \pm 0.002$, $X_Q \approx 0.284 \pm 0.005$, $\Delta X_S \approx 0.050 \pm 0.001$, mainly due to uncertainties in the analysis part. Therefore, for each experiment three reactor samples were taken, diluted with buffer solution and analyzed. The reproducibility between series of experiments was somewhat less (± 0.005), due to possible variations in the synthesis of the reactants, small temperature differences or a slightly different feedpoint position. Mass balances (for B) were checked and were found to be accurate ($\pm 98\%$ was recovered in the products) for the experiments in aqueous buffer solutions.

3.4. Experimental conditions

Typical reaction conditions are listed in Table I. For the suspension experiments with varying holdups, the volume of the Naphthol solution was always kept constant. The suspensions of glass beads were prepared by adding the appropriate amount of solids to the Naphthol solutions. In order to keep the total molar ratio of A and B constant, the amount of B-solution fed to the reactor had to be adapted. For the glass beads sieved fractions were used with a rather narrow size distribution, as determined with a Microtrax X100 Particle Analyzer. Adsorption of reactants and products on the glass beads was found to be negligible and, therefore, did not

influence the observed product distribution. This was checked by ‘extracting’ typical, well-known, reaction mixtures with the glass beads concerned and analyzing again the reaction mixture. The distribution coefficients were roughly estimated to be in the order of magnitude of $1-5 \times 10^{-8}$ mol/m² glass beads and S appears to be slightly preferentially absorbed. For a typical experiment the X_S values will be underestimated by some 0.0001 unit due to adsorption. Therefore, no disturbing effect on the results is to be expected owing to adsorption phenomena on the solid particles.

The liquids selected for the dispersion study were octanol and heptane, because of their difference in naphthol solubility. Distribution coefficients for the individual components were obtained from extraction experiments, but the accuracy of the separate coefficients for both *o*-R and *p*-R respectively was relatively low. Therefore, the mono-azo compounds were regarded as one component in the analysis of these experiments.

4. Results

4.1. Critical feed rate

First, the critical feed times for the operation conditions of Table 1 were identified. The critical feed time, above which the product distribution for the given amount of reactant does not depend longer on the injection time, is within the range 200–500 s for all conditions considered. A feed time of 1200 s (corresponding with a feed rate of 30 ml/h) was chosen safely above the critical feed times determined.

4.2. Single-phase experiments

Before the start of the multiphase experiments several series of single-phase experiments were performed. The Engulfment model by Baldyga and Bourne (1989) was used to recalculate local energy dissipation rates from experimentally determined X_S and X_Q values at different stirrer speeds, it was found that for $N > 500$ rpm the relative energy dissipation rate, i.e. the ratio between the calculated and the average energy dissipation rate ($\varepsilon_{av} = CN^3 d_{st}^5 / V_L$) remains essentially constant, indicating that the reaction is localized in a zone of more or less homogeneous energy dissipation. Indications of the thus derived relative energy dissipation rates are presented in Fig. 1.

4.3. Two-phase experiments: Effect of a dispersed gas phase

The effect of the presence of gas bubbles on the product distribution in a sparged stirred tank, operating in the impeller-flow dominated regime, is not clear

Table 1
Typical reaction conditions

Temperature	298	(K)
pH	9.9	dimensionless
Volume Naphthol solution	500–1000	(ml)
Injected volume B-solution	10	(ml)
Feed rate reactant B	30	(ml/h)
Concentration $C_{B,0}$	40	(mol/m ³)
Concentration $C_{A,0}$	1.04	(mol/m ³)
Stirrer speed	100–1200	(rpm)

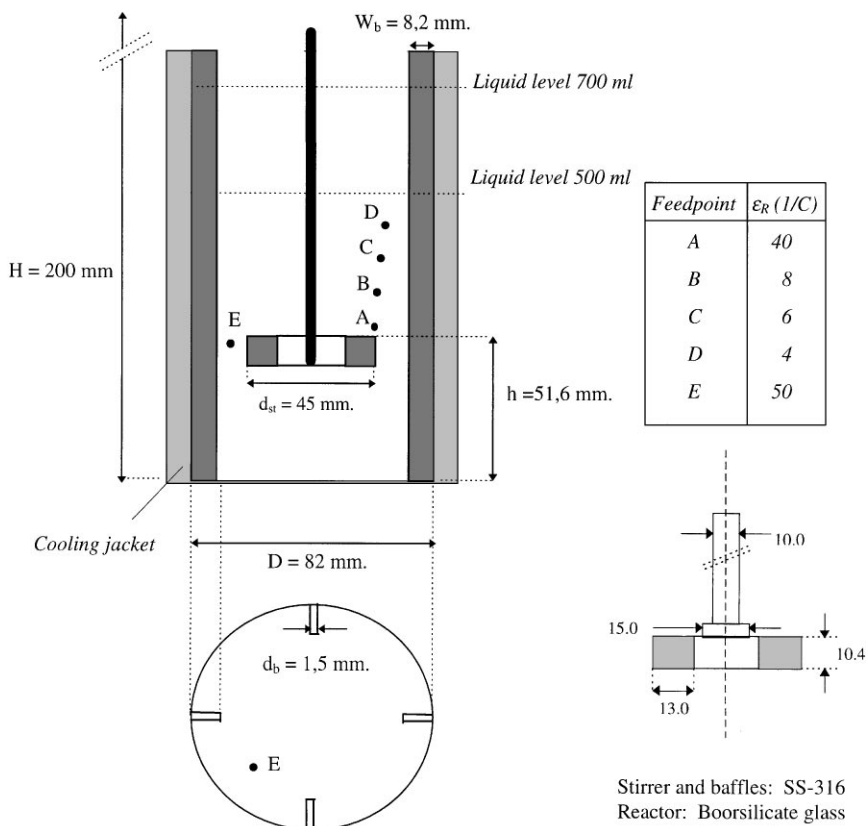


Fig. 1. Experimental setup.

beforehand. Fort et al. (1994) found a suppression of the energy dissipation rate in the impeller discharge flow and an increase in the remaining part of the agitated vessel. This would imply a position-dependent effect of sparging on the X_S value obtained. Gas sparging experiments were performed for two different feedpoints, using Nitrogen and SF_6 as dispersed phase, see Fig. 2.

The effect of sparging or gas entrainment, thus the presence of gas bubbles, on the product distribution for the mixing sensitive test reaction seems to be limited from the results of this work. The minor effects found are, however, in accordance with the results of Fort et al. (1994); the X_S value for feedpoint C slightly decreases (thus suggesting a slightly increased local energy dissipation rate), whereas the X_S value for one of the series at a superficial gas velocity of 2.8×10^{-2} m/s for feedpoint A just above the stirrer increased from 0.061 to 0.063 (ca. 3% increase), corresponding to a decrease of approximately 1.7 W/kg (ca. 7%) in the apparent local power input, as was recalculated using the E-model. This latter result is in line with the expected reduced power input by agitation due to the decreased density of the dispersion. The decrease in the apparent local power input corresponds with the gas holdup, which was also estimated to be 7%, using the correlation of Takenaka and Takahashi (1992).

4.4. Two-phase experiments: Effect of a dispersed solid phase

In Fig. 3 the results are presented of experiments with different holdups of solid particles at constant total volume for two different particle sizes. By using effective properties for viscosity and density for the slurries in the E-model it was investigated if the measured variation in product distribution at increasing holdup can be described (see Fig. 3). The series with the 290 μm particles at 500 rpm (and 500 ml total volume) seems to differ significantly from the other series, since no effect on X_S was found. This may be explained by insufficient suspension of these solid particles at these conditions. Since the feedpoint is located above the stirrer probably the local solids holdup was insufficient to produce any effect. It appears that a reasonable prediction of the experimental trend for the other three series is obtained by just implementing the effective viscosity, thus using $E = E(\text{II})$ (Eq. 9). This result was confirmed for duplicate series using the 1-Naphthol + 2-Naphthol system.

Experimental series like those presented in Fig. 3 are measured using a freshly prepared stock of diazotized sulfanilic acid per series and the experiments within a series are performed in random order of

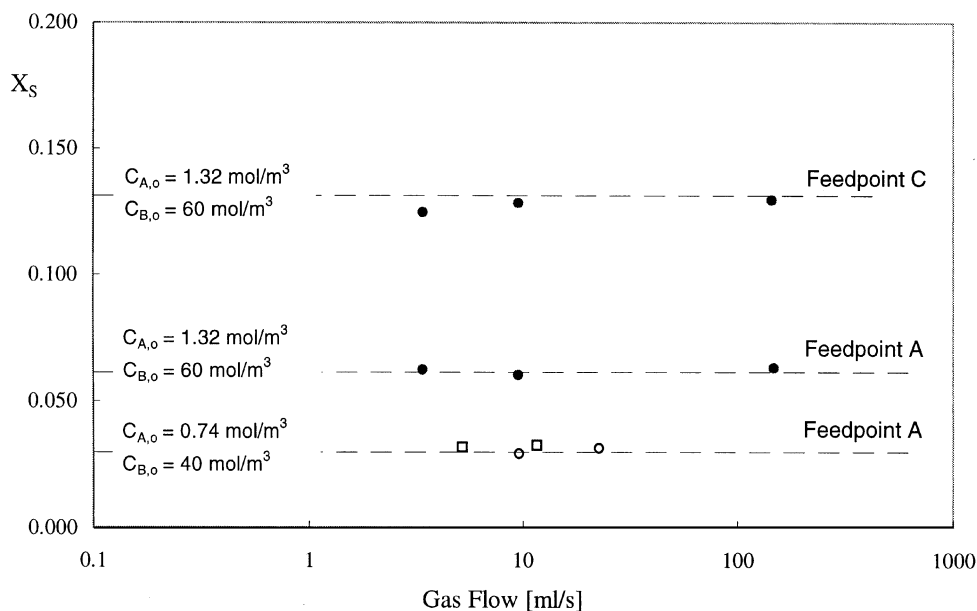


Fig. 2. Effect of gas bubbles ● gas phase = N_2 , $N = 700$ rpm, $V_L = 700$ mL, $\varepsilon_G = 1-7$ vol%, □ gas phase = SF_6 , $N = 900$ rpm, $V_L = 700$ mL, $\varepsilon_G = 1-3$ vol%, ○ gas phase = N_2 , $N = 900$ rpm, $V_L = 700$ mL, $\varepsilon_G = 1-3$ vol%, - - - X_S values homogeneous liquid phase.

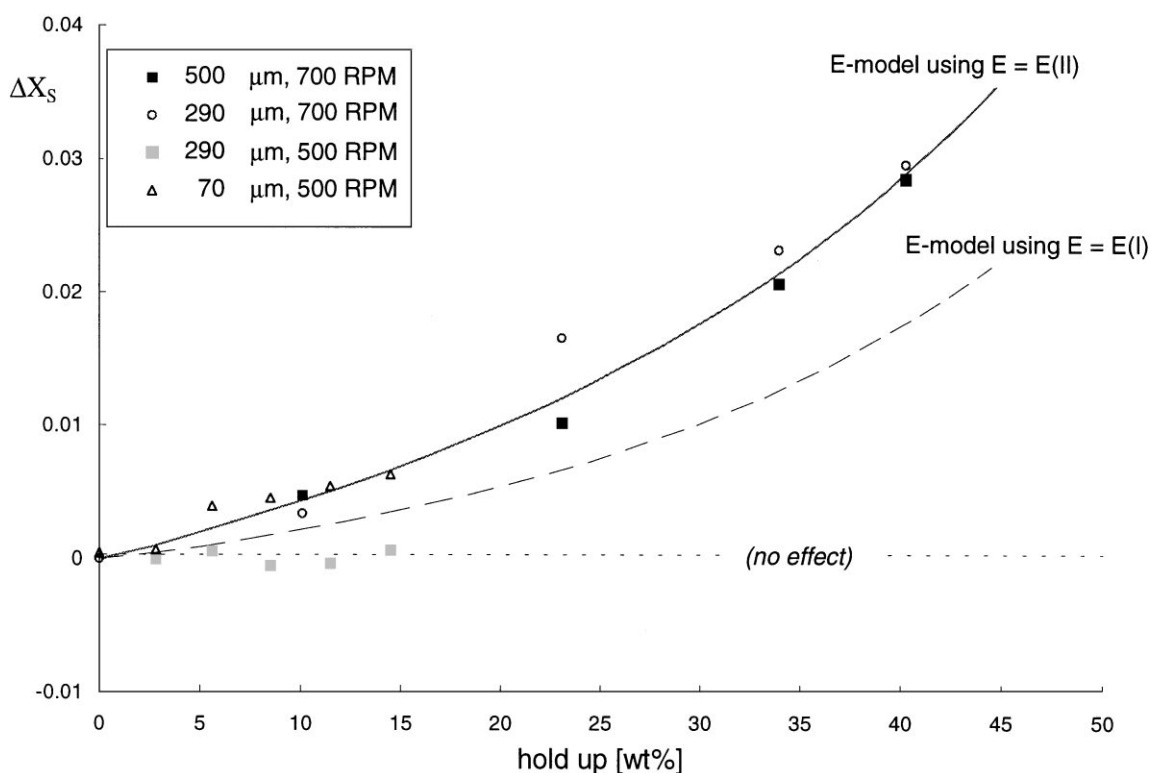


Fig. 3. Glass beads holdup variation for feedpoint C, 1-Naphthol system, $c_{A,o} = 1.04$ mol/m³, $c_{B,o} = 40$ mol/m³. Solid and dashed line are E-model simulation results using Eqs. (9) and (8), respectively.

holdup, starting and ending with a blank run (zero holdup), in order to exclude time-dependent trends. Mass balances were found to be satisfied within 0–4% deviation of the theoretical maximum amount of B injected. For a single data series (not shown in the

figures) with 3 mm particles the X_S -value was found to decrease (from $X_S = 0.07$ at zero holdup to 0.06 at 5 wt% holdup and 990 rpm, $C_{A,o} = 1.32$ mol/m³, $C_{B,o} = 60$ mol/m³, $V_{A,o} = 500$ mL, $V_{B,o} = 10$ mL at feedpoint E).

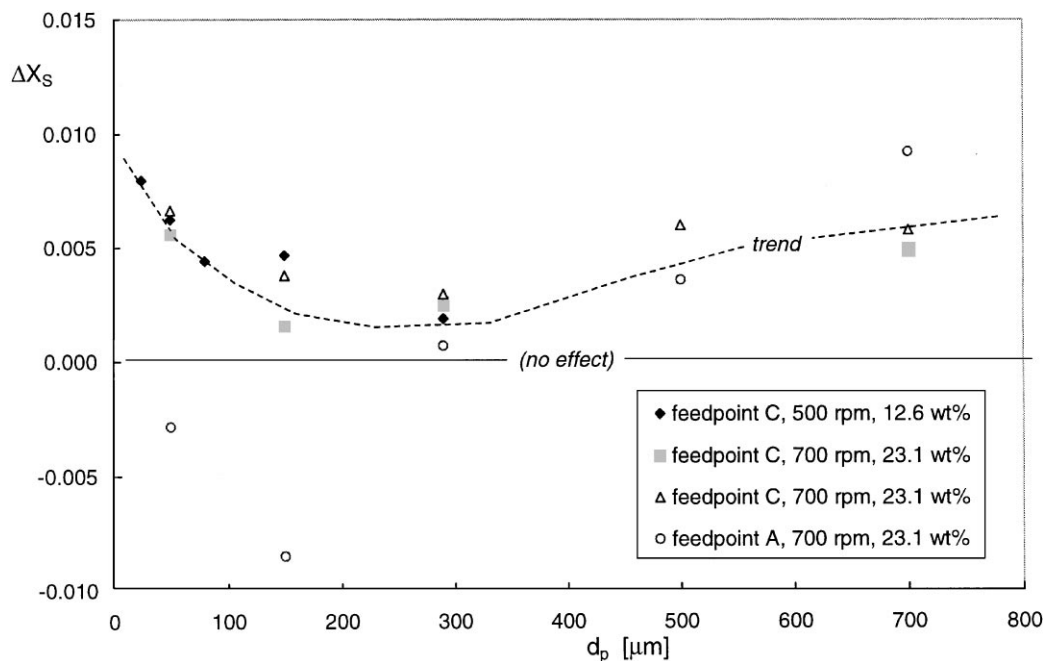


Fig. 4. Solids particle size variation at constant holdup, $V_L = 500$ ml, $c_{A,o} = 1.04$ mol/m³, $c_{B,o} = 40$ mol/m³.

The average particle size has been varied at constant holdup. Results for the 1-Naphthol system are presented in Fig. 4. With the 1- + 2-Naphthol system similar results were found (not shown). The trend observed, represented by the dashed line, is approximately within the experimental accuracy, however, the presented trend could be recognized clearly for all individual series. The experiments were, as stressed before, conducted randomly with respect to particle size. For very small particles the dispersion behaves as a pseudo-fluid with the appropriate effective (density and viscosity) properties. Energy is probably mainly dissipated by particle–particle interaction. This will decrease due to a strong reduction in the number of ('near-') collisions with increasing particle size, at constant holdup. In the classification by Elgobashi (1994) for the *two-way* coupling regime the regime transition between 'particles enhancing energy dissipation' and 'particles enhancing energy production' is approximately given by $\tau_p/\tau_k \approx 10^2$. For the glass beads used under the experimental conditions applied, the transition is located at approximately 150 μm . This is in agreement with the experimentally determined decrease in the X_s value going from particles of 50 to 150 μm , as shown in Fig. 4. However, the volume fractions used in this study are such that all experiments are conducted in the '*four way coupling*'-regime, according to Elgobashi (1994).

The increase at higher particle sizes may be caused owing to the fact that the particles are being less able to follow fluid motion (an increase in particle response time) and more energy is required to (re-) suspend the particles

(see, e.g., Zwietering (1958)) and more energy is dissipated in particle–particle collisions and particle–wall collisions. Another explanation may be an increase in the amount of stagnant liquid moving with the particles.

A similar result for the turbulence intensity at different particle diameters has been presented in an overview by Zakharov et al. (1993) for gas–solid two phase flow at low concentrations (< 1 vol% solids). In their study friction drag due to the flow of a dispersion was studied at constant dispersed phase holdup for different particle size. It was found that first the drag was reduced with increasing particle diameter and, with a further increase in diameter the drag started increasing again. The particle regime for which friction reduction may occur was estimated in their study using the Owen theory, assuming that (quote:) 'friction reduction is possible in a flow laden with particles having a relaxation time which is higher than the characteristic time of the energy-containing vortices, but which does not exceed the characteristic time of the maximum possible vortices'. Applying these criteria to the conditions of current investigation, glass particles of 150–1000 μm may 'decrease the friction', implying that for these particles the turbulence intensity will be increased or less reduced.

The results of this study are in accordance with those presented by Guichardon et al. (1995), who found a negligible influence of solid particles ($\rho = 2500$ kg/m³, $d_p = 27, 201, 1250$ μm) on the micromixing index for their (iodide-iodate) test reaction in the range 1–6 wt%. The scatter of the experimental data of Barresi (1997) in combination with the limited effect of solids makes

Table 2
Distribution coefficients for reactants and products

$(m = c_{\text{disp. phase}}/c_{\text{buffer}})$	Heptane m dimensionless	Octanol m dimensionless
1-Naphthol	0.9	2.10 ²
<i>o</i> R	0.12	1.1
<i>p</i> R	0.0010	0.06
R(<i>o</i> R + <i>p</i> R)	0.020	0.2
S	0.19	0.09

comparison with the results of the present study difficult, though the results are not necessarily conflicting. Scouting experiments in this study with 5 wt% solids of different density (not shown in figures), comparing glass beads with polystyrene, polypropylene and polymethyl methacrylate beads of the same size at 5 wt% holdup, showed no significant influence of particle density and within the experimental error, which was larger due to product adsorption on the plastic beads.

4.5. Two-phase experiments: Effect of a dispersed liquid phase

A dispersed liquid phase may influence the obtained product distribution in different ways. Besides possible effects on the state of local mixing, which can be signifi-

cant as was shown in experiments with the solid particles, mass transfer can be important and macroscopic hydrodynamics may change. In this work the results of scouting experiments with two different liquid phases are reported. As dispersed phase a solvent-grade heptane containing heptane isomers (82%), octane (15%) and toluene (3%), analytical grade (99 + % purity) heptane and octanol (99 + % purity) were used. For these solvents the (approximate) distribution coefficients for the reactants and products were determined by extraction experiments, see Table 2. Heptane was selected for its low affinity for 1-Naphthol (thus essentially excluding mass transfer effects), whereas octanol was chosen as a solvent showing a high Naphthol affinity.

In Fig. 5 two sets of experiments for different holdups of heptane are presented. Optically, the dispersed phase was distributed homogeneously throughout the dispersion volume for stirrer speeds exceeding 450 rpm. From simulations for the series at feedpoint A, it seems that taking the effective viscosity (for solid spheres!) according to Graham's relation (1981) yields better results for these conditions than the correlation by Vermeulen (Perry, 1988) for liquid–liquid dispersions in baffled agitated tanks. Conclusions with respect to the effective viscosity for liquid–liquid dispersions at higher holdups can, however, not be drawn from these results, considering the assumptions by using the E-model extended with mass transfer. This is especially true for the octanol data series, where de-localization of the reaction zone dominates.

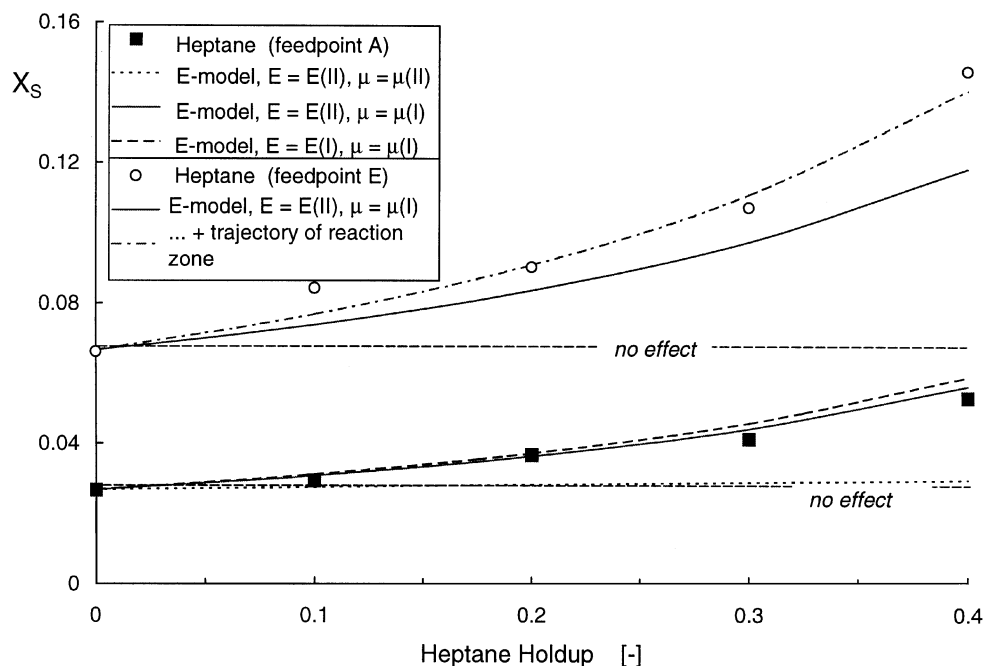


Fig. 5. Experiments with heptane as dispersed phase at different volume fractions.

Series I: Feedpoint A, $C_{A,o} = 1.04 \text{ mol/m}^3$, $C_{B,o} = 40 \text{ mol/m}^3$, 700 ml, 1000 rpm.

Series II: Feedpoint E, $C_{A,o} = 1.32 \text{ mol/m}^3$, $C_{B,o} = 60 \text{ mol/m}^3$, 500 ml, 500 rpm. Simulation input: $\mu(\text{I}) \Rightarrow$ relative viscosity according to Graham (1981), $\mu(\text{II}) \Rightarrow$ relative viscosity according to Vermeulen (Perry, 1988, Eqs. (21)–(32), changing ε_R along trajectory of reaction zone according to Yu (1993).

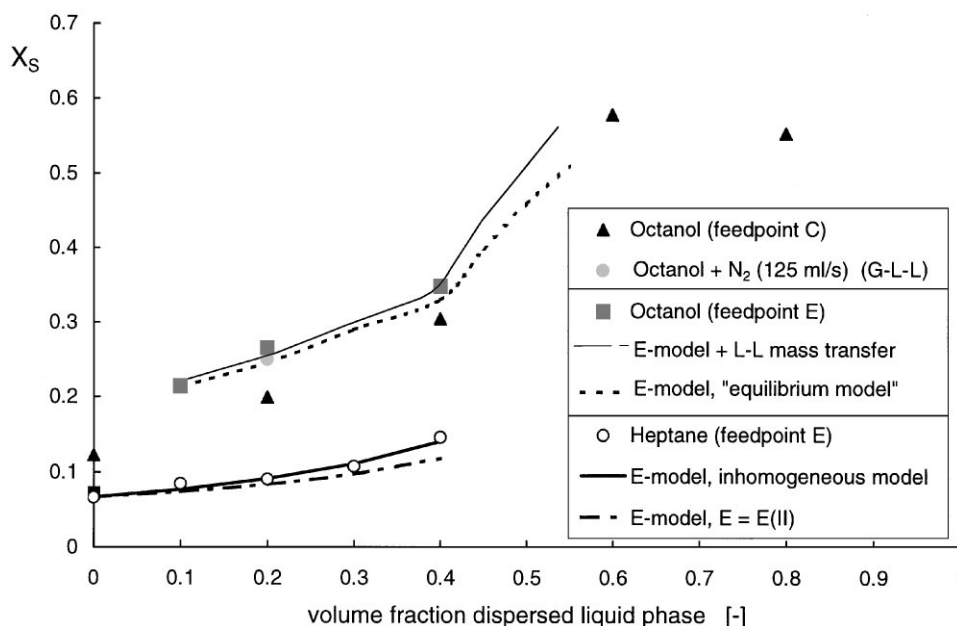


Fig. 6. Experiments with octanol and heptane as dispersed phase at increasing holdup and $C_{A,0} = 1.32 \text{ mol/m}^3$, $C_{B,0} = 60 \text{ mol/m}^3$, 500 ml, $N = 500 \text{ rpm}$ and simulation results assuming $m_A = 100$, $\varepsilon_R = 1$ and using the viscosity correlation according to Graham (1981) and $E = E(\text{II})$, see Eq. (9), for the E model.

For the experiment series at feedpoint E the simulation results started deviating from the experimental data at higher holdups. This is most likely caused by a delocalized reaction zone. Due to the distribution of Naphthol over both liquid phases the number of engulfments required for complete reaction of a feedlump slightly increases, causing the reaction to take place in zones of different energy dissipation. This effect is more important for feedpoint E in the radial flow leaving the impeller zone than for feedpoint A in the suction stream to the impeller zone.

This effect is even more pronounced in case octanol is used. Fig. 6 shows two octanol data series for different feedpoints. Since Naphthol is extracted to a large extent by the octanol, the number of engulfments required for complete reaction of a feedlump is such that the average energy dissipation rate, as experienced by the reaction zone, is essentially the average energy dissipation rate for the complete tank, ε_{av} . Assuming this, the E-model extended with mass transfer was used to see if the experimental results could be described. Although the set of experimental data is limited, the results seem promising. Using the effective dispersion viscosity in the Engulfment model seems to yield reasonable description of X_S values at increasing holdup, both for the viscosity correlation's of Graham (1981) and Vermeulen (Perry, 1988). It should be noted that in the experiments described the mass transfer rate is relatively unimportant (as the 'equilibrium model', i.e. the model without mass transfer limitations by using an extremely high mass transfer coefficient k_{LL} in the model and presented by the dotted line in

Fig. 6, gives almost identical results as the model including mass transfer), due to the low feed rate of reactant B. More (and dedicated) experiments are required to investigate (or validate) the mass transfer description.

5. Discussion and conclusions

In this study for a limited set of experimental conditions the effect of the presence of bubbles, drops and solid particles on the product distribution for the (micro-)mixing sensitive diazo-coupling reaction (Bourne et al., 1981) is investigated. The diazo-coupling reaction system can be used conveniently for this purpose. Adsorption on glass beads is found to be negligible and the dispersed phases used do not seem to affect the intrinsic reaction kinetics and product analysis. The single-phase experiments could be satisfactorily described using the Engulfment model, and this model was tested on its applicability in the multiphase systems. In the presence of gas, liquid and solid particles in the continuous liquid phase, the product distribution could reasonably well be described by the Engulfment model, if effective dispersion slurry properties are implemented. Modification of local liquid-phase turbulence, or the kinetic energy spectrum, at a scale relevant for the test reaction, is then accounted for.

For the liquid-liquid dispersions the viscosity correlation seems less established. From the limited set of experiments, it appears that application of the viscosity correlation of Graham (1981) for liquid-solid

applications yields acceptable results for heptane-buffer dispersions at the conditions considered in this work (a.o. heptane holdup ≤ 40 vol%). Additional experimental work is, however, recommended.

In the work presented, the mass transfer rate was relatively unimportant for the liquid–liquid dispersions and only preliminary experimental results and a simple mass transfer model have been presented. Further research of the combined effects of the mass transfer rate and mixing rate is desired for the development of multi-phase reactor models.

Acknowledgements

The authors wish to thank B. Knaken for constructing the experimental setup and A.K. Jellema and W. Hesselink for their valuable contribution to the experimental work. The Shell Research and Technology Centre, Amsterdam (The Netherlands) is acknowledged for the financial support.

Notation

A_{LL}	interfacial area, m^2
c	concentration, mol/m^3
C	configuration-dependent power constant, dimensionless
D	diffusion coefficient, m^2/s
d_p	particle diameter, m
d_{st}	stirrer diameter, m
E	engulfment rate, $1/s$
k_i	partial mass transfer coefficient, m/s
k_{LL}	overall liquid–liquid mass transfer coefficient, m/s
m_i	distribution coefficient ($c_{d,i}/c_{c,i}$) _{equilibrium} , dimensionless
N	stirrer speed, $1/min$
R_i	source term for chemical reaction, $mol\ i/m^3\ s$
Sh	Sherwood number ($= k_i d_p / D$), dimensionless
Sc	Schmidt number ($= \nu / D$), dimensionless
t	time, s
t_{feed}	feed time of a fixed amount of reactant solution, s
V	volume, m^3
X_S	product distribution parameter (defined in Eq. (3)), dimensionless

Greek letters

ε_{av}	average energy dissipation rate W/kg
ε_R	relative energy dissipation rate ($= \varepsilon / \varepsilon_{av}$) dimensionless
λ_K	Kolmogoroff length scale ($= (\nu^3 / \varepsilon)^{1/4}$) m
μ	dynamic viscosity, $kg/m\ s$

ν	kinematic viscosity, m^2/s
ρ	density, kg/m^3
σ	number of feed lumps in E model, dimensionless
τ_K	Kolmogoroff time-scale ($= (\nu / \varepsilon)^{1/2}$) s
τ_p	particle response time ($= \rho_p d_p^2 / (18 \rho_c \nu)$) s

Superscripts and subscripts

A	1-Naphthol
AA	2-Naphthol
B	diazotized sulfanilic acid
c	continuous liquid phase
d	dispersed phase
eff	effective dispersion property
$inside$	inside
0	initial value
$outside$	outside
p	particle
r	effective

References

- Baldyga, J., & Bourne, J.R. (1988). Calculation of micromixing in inhomogeneous stirred tank reactors. *Chem. Engng Res. Des.*, 66, 33–38.
- Baldyga, J., & Bourne, J.R. (1989). Simplification of micromixing calculations: 1. Derivation and application of new model. *Chem. Engng J.*, 42, 83–92.
- Baldyga, J., & Pohorecki, R. (1995). Turbulent micromixing in chemical reactors – a review. *Chem. Engng J.*, 58, 183–195.
- Barresi, A.A. (1997). Experimental investigation of interaction between turbulent liquid flow and solid particles and its effects on fast reactions. *Chem. Engng Sci.*, 52, 807–814.
- Bennington, C.P.J., & Bourne, J.R. (1990). Effect of suspended fibers on macro-mixing and micro-mixing in a stirred tank reactor. *Chem. Engng Commun.*, 92, 183–197.
- Bennington, C.P.J., & Thangavel, V.K. (1993). The use of a mixing-sensitive chemical reaction for the study of pulp fiber suspension mixing. *Can. J. Chem. Engng*, 71, 667–675.
- Bourne, J.R., Kozicki, F., & Rys, P. (1981). Mixing and fast chemical reaction-I: Test reactions to determine segregation. *Chem. Engng Sci.*, 36, 1643–1648.
- Bourne, J.R., Kut, O.M., Lenzner, J., & Maire, H. (1990). Kinetics of the diazo coupling between 1-Naphthol and diazotized sulfanilic acid. *Ind. Engng Chem. Res.*, 29, 1761–1765.
- Bourne, J.R., & Thoma, S.A. (1991). Some factors determining the critical feed time of a semi-batch reactor. *Trans. I. Chem. E.*, 69, Part A, 321–323.
- Bourne, J.R., Kut, O.M., & Lenzner, J. (1992). An improved reaction system to investigate micromixing in high-intensity mixers. *Ind. Engng Chem. Res.*, 31, 949–958.
- Calderbank, P.H. (1967). Gas absorption from bubbles. *Chem. Engng*, 45 (10), 209–233.
- Elgobashi, S. (1994). On predicting particle-laden turbulent flows. *Appl. Sci. Res.*, 52, 309–329.
- Falbe, J. (1980). New synthesis with carbon monoxide (Ch. V.) In H. Bahrman (Ed.). *Koch reactions*, Berlin: Springer.
- Fort, I., Machoñ, V., & Kadlec, P. (1994). Distribution of energy dissipation rate in an agitated gas–liquid system. *Chem. Engng Technol.*, 16, 389–394.

- Gore, R.A., & Crowe, C.T. (1989). Effect of particle size on modulating turbulent intensity. *Int. J. Multiphase Flow*, 15, 279–285.
- Graham, A.L. (1981). On the viscosity of suspensions of solid spheres. *Appl. Sci. Res.*, 37, 275–286.
- Guichardon, P., Falk, L., Fournier, M.C., & Villermaux, J. (1995). Study of micromixing in a liquid–solid suspension in a stirred reactor. *A.I.Ch.E. Symp. Ser.* 305, 91, 123–130.
- Hetsroni, G. (1989). Particle-turbulence interaction. *Int. J. Multiphase Flow*, 15, 735–746.
- Kada, H., & Hanratty, T.J. (1960). Effects of solids on turbulence in a fluid. *A.I.Ch.E. J.*, 6, 624–630.
- Lenzner, J. (1991). *Der Einsatz Rascher Kompetitiver Reaktionen zur Untersuchung von Mischeinrichtungen*. Ph.D. thesis No. 9469, ETH Zürich.
- Perry, R.H., & Green, D.W. (1988). *Chemical engineers handbook*. New York: McGraw-Hill.
- Schreck, S., & Kleis, S.J. (1993). Modification of grid-generated turbulence by solid particles. *J. Fluid Mech.*, 249, 665–688.
- Takenaka, K., & Takahashi, K. (1992). Local gas holdup and gas recirculation rate in aerated vessel equipped with a Rushton turbine impeller. *J. Chem. Engng Japan*, 29, 799–804.
- Tsuji, Y., Morikawa, Y., & Shiomi, H.H. (1984). LDV measurements of an air-solid two-phase flow in a vertical pipe. *J. Fluid Mech.*, 139, 417–434.
- Villermaux, J., Falk, L., & Fournier, M.C. (1994). Potential use of a new parallel reaction system to characterize micromixing in stirred reactors. *A.I.Ch.E. Symp. Ser.* 292, 90, 50–54.
- Yu, S. (1993). *Micromixing and parallel reactions*, Ph.D. thesis No. 10160, ETH Zürich.
- Zwietering, Th. N. (1958). Suspending of solid particles in liquid by agitators, *Chem. Engng Sci.*, 8, 244–253.